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A review on microwave assisted pyrolysis of coal and biomass for fuel production

Faisal Mushtaq [a,c], Ramli Mat [a], Farid Nasir Ani [b,*]

[a] Faculty of Chemical Engineering, Universiti Teknologi Malaysia, UTM 81310, Skudai, Johor Bahru, Johor Darul T'azim, Malaysia
[b] Department of Thermodynamics and Fluid Mechanics, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, UTM 81310, Skudai, Johor Bahru, Johor Darul T'azim, Malaysia
[c] Faculty of Engineering, Department of Chemical Engineering, Balochistan University of Information Technology, Engineering and Management Sciences, Airport Road, Baleli, Quetta, Balochistan, Pakistan

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ABSTRACT

The energy insecurity from oil and natural gas and increased CO_2 emission from fossil fuels is driving societies to look for sustainable and renewable energy supply. The huge coal resources can serve as a potential source for fuels. Bio-energy from biomass has been recognized as renewable energy to reduce CO_2 emission. Although fast pyrolysis has emerged as the most promising technology to convert organic materials to liquid fuels at shorter duration but it still faces some technical challenges in improving product yield, its quality and process energy efficiency. Microwave assisted pyrolysis of coal and biomass in the presence of microwave absorber provides distinctive environment to resolve these challenges. The microwave absorber can indirectly heat coal and biomass particles which are relatively microwave transparent and influence product yield and its quality by contributing as a catalytic precursor. The microwave heating of coal or biomass particles with microwave absorber shows efficient heating and sufficient contact of volatile or gas phase species with specific microwave absorber can improve fuel quality.

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* Corresponding author. Tel.: +60 7 5534715; fax: +60 7 5566159.
  E-mail address: farid@fkm.utm.my (F.N. Ani).

1. Introduction

The conventional oil and Natural Gas (NG) fuel resources have been playing a vital role in shaping the socioeconomic status of the society. The conventional fuel resources are valuable supply of finite natural energy. However, their increasing supply and exploited production have shown great concern over fuel source depletion. In addition, increasing contribution of fossil fuels has augmented CO_2 emission. Presently, the biggest challenge faced by the oil and gas sector is how to sustain production from currently producing fields [1]. Global oil and NG resources are considered as one of the quickly depleting natural energy in future. However, substantial contribution of coal, bio-fuels and waste can play a vital role to the world energy in future.

Coal still remains the largest and cheapest source of solid fuel across the globe [2,3]. It is primarily used as a fuel source for power generation [4]. Moreover, with the development of industrial sector and increased energy demand in developing countries, more coal is being used [5]. The increasing dependence on coal to produce electricity may not be the only option in the proper utilization of coal. The sustainable utilization of coal presents a prospect to the global research and development efforts with strong emphasis on inexpensive energy supply, which is compounded with CO_2 reduction. The huge recoverable coal resources can be used to produce synthetic liquid fuels and chemical feedstock, which can serve as a partial replacement to oil and NG. Besides coal, biomass resources have been identified as renewable and sustainable feedstock to recover energy products. Moreover, waste biomass is available in abundant quantity across many parts of the world and is considered environmentally friendlier due to its CO_2 neutrality. Energy can be recovered from waste biomass by direct combustion to produce heat and power or converting it to more valuable forms, such as liquid and gas fuels by fast pyrolysis.

Besides fast pyrolysis, Microwave Assisted Pyrolysis (MWAP) provides distinctive heating method to process variety of feedstocks and is also suitable for producing liquid and gas fuel products from coal and biomass. Coal is essentially transparent to Microwave (MW) due to its fairly low MW absorption capacity. This low MW absorption of coal signifies the major stumbling block during MWAP [6], although some moisture and mineral contents within coal matrix respond more readily to MW energy. Moreover, the coal sample cannot be pyrolyzed or attain sufficient temperature without Microwave Absorber (MWA) even in the presence of high MW power source [7]. However, carbonaceous, metallic or inorganic substances and even metal are capable of increased MW assimilation capacity, which can be used with coal to increase its MW absorption capacity [7–12]. Waste biomass shows some improved MW absorption capacity due to the presence of high moisture and inherent inorganic substances. However, in the absence of MWA, product yield from waste biomass requires considerable MW power and time to reach pyrolysis temperature [13,14], and heating rate achieved at the expense of higher MW power is fairly low. Therefore, suitable MWA is required with waste biomass to achieve high temperature and reduce pyrolysis time at lower MW power. Certain carbon

based materials, metal oxides and inorganic additives are capable of converting good amount of MW energy to thermal energy, which can be transmitted to waste biomass material. More importantly, some MWA provide in-situ upgrading of pyrolysis vapors by increasing product selectivity in bio-oil, thereby significantly reducing the cost associated with downstream bio-refining.

This review aims to present progress in global fossil fuel energy scenario and global oil, NG and coal production, and global CO_2 emission trends from oil, NG and coal sectors. More importantly, reserves to production ratio of global proven oil, NG and coal reserves are offered to address energy insecurity. The product distribution from microwave pyrolysis of coal and waste biomass is compared with conventional pyrolysis under comparable conditions. The MWAP of coal with carbonaceous and metal oxide absorbers and metals along with MWAP of waste biomass without absorber and with carbonaceous absorbers, inorganic and metal oxide additives are reviewed keeping in view the critical influential process factors. The co-utilization of coal and biomass through conventional co-gasification and co-pyrolysis routes is reviewed to observe synergetic effects to improve fuel products. Finally, MWAP of coal and waste biomass factor considerations and concerns are summarized by analyzing their association on temperature, heating rate, product yield and composition, and some future directions are suggested.

2. Global fossil energy scenario

The global primary energy comes from non-renewable fossil fuel resources. The global Total Primary Energy Supply (TPES) reached 12,717 Metric tonnes of oil equivalent (Mtoe) by end-2010 and an increase of 107% from 1973 to 2010. Petroleum oil and NG accounted for the largest collective share of 54%, followed by coal and peat of 27%, bio-fuels and waste 10%, nuclear, hydro, geothermal, solar-photo voltaic, wind, and heat etc. of 9% to the world TPES by end-2010. On the other hand, global Total Primary Energy Consumption (TPEC) was estimated at 8677 Mtoe in end-2010 and rose to 86% from 1973 to 2010. Petroleum oil shared 41% and the share of NG was recorded the highest at 15% to global TPEC by end-2010. Bio-fuels and waste contributed to the third largest share of 13% after NG and oil. However, the coal consumption remained fairly constant to about 10% [15,16]. In addition, the world TPEC was estimated at 495 quadrillion British thermal units (Btu) in 2007 and is expected to increase 590 quadrillion Btu in 2020, and 739 quadrillion Btu by 2035, an increase of 49% from 2007 to 2035 [17]. The progress in global production from oil, NG and coal resources from 1981 to 2012 is shown in Fig. 1. The global coal production was observed at same level of oil by end-2012. The share of NG, coal and oil increased to 129%, 107% and 41%, respectively, from end-1981 to end-2012. The increasing production from fossil fuel resources shows great concerns over global CO_2 emission trends and life expectancy of global proven fossil fuel reserves.

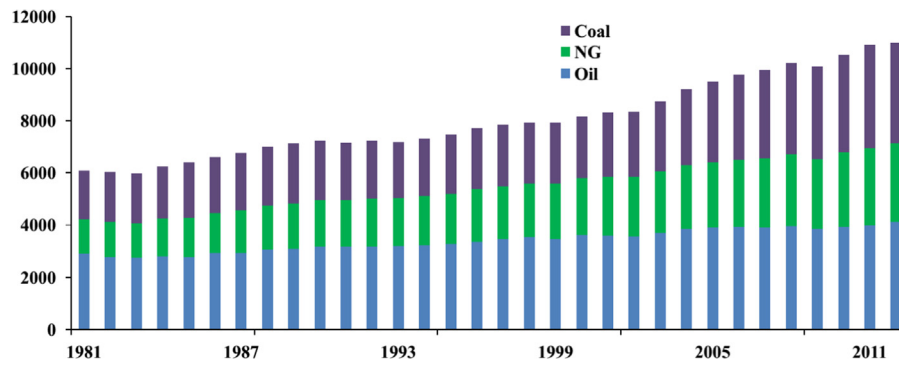**Fig. 1.** Progress in global fossil fuel production in Mtoe (data extracted from [3]).
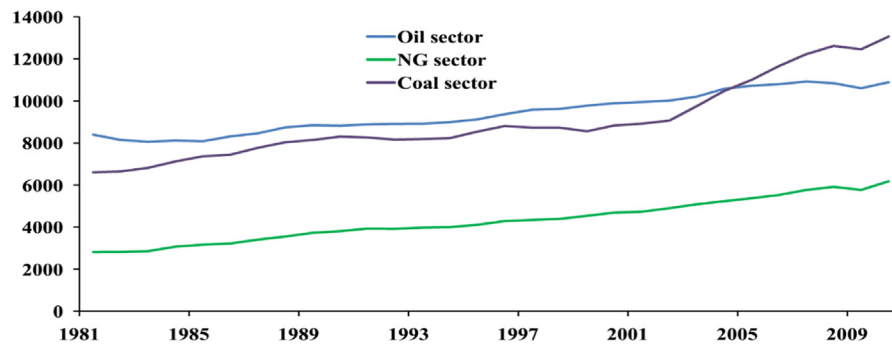

Fig. 2. Global CO_2 emission from three sectors in Mt of CO_2 (data extracted from [22]).
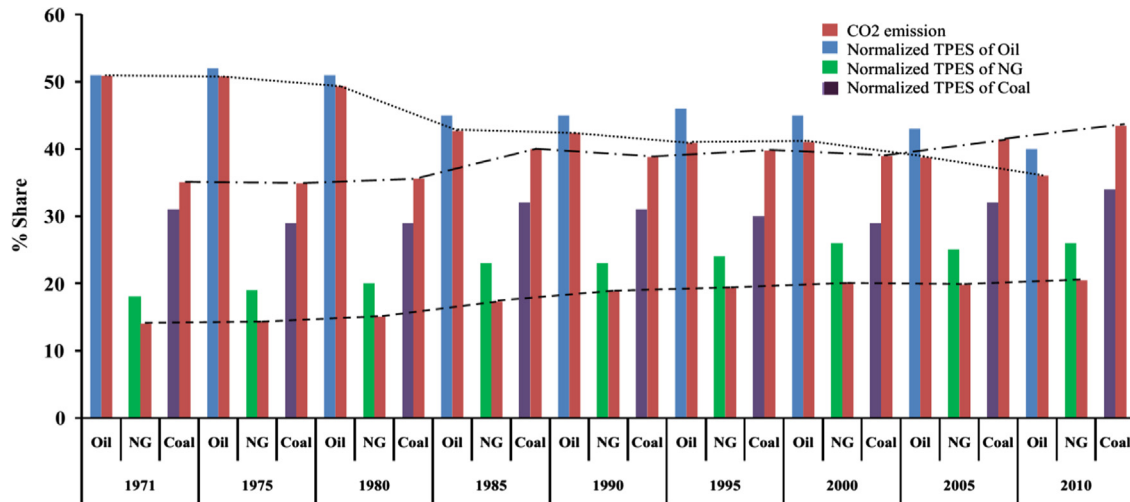

Fig. 3. Progress in global total primary energy supply and global CO_2 (data extracted from [16]).
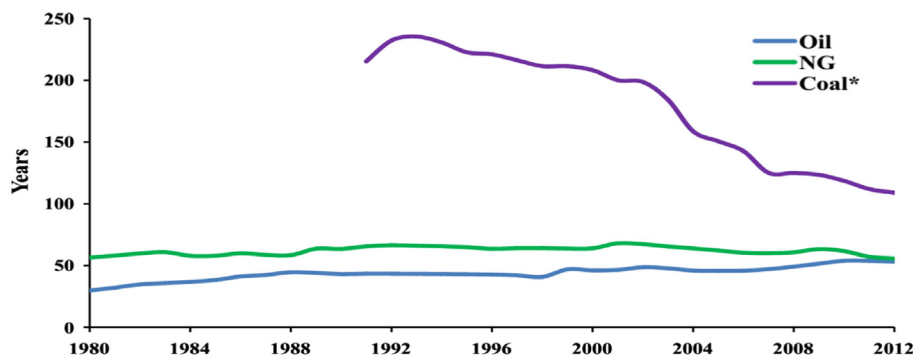

Fig. 4. Progress in global reserves to production ratio of fossil fuels (data extracted from [3]).

2.1. Global CO$_2$ emission

The use of fossil fuels as a fuel source is associated with various atmospheric pollutions, but CO$_2$ emission from fuel combustion has contributed as a major precursor in green house effect by trapping sun heat resulting in sharp rise in the earth surface temperature [18]. Moreover, increased concentration of green house gases particularly from CO$_2$ can contribute to increased sea levels due to melting of ice caps and sheets [19]. The global CO$_2$ emission rose to 30.33 Giga tonnes (Gt) of CO$_2$ equivalent in 2010, an increase of 52% in 1990 [20]. Moreover, the fossil fuels combustion generated a record global CO$_2$ emission of 32 Gt by end-2011, an increase of 1 Gt in 2010, or 3% [21]. According to BP statistical review of world energy, the global CO$_2$ numbers are even higher and estimated at 34.47 Gt of CO$_2$ by end-2012, an increase of 1.9% from 2011 to 2012 [3]. The global CO$_2$ emission from oil, NG and coal sectors in Metric tonnes (Mt) of CO$_2$ from 1981 to 2010 is shown in Fig. 2. The increased CO$_2$ emission from coal sector can be associated to increased global coal production. The development in global TPES and global CO$_2$ footprints from oil, NG and coal utilization is shown in Fig. 3. The global CO$_2$ emission from oil dominated from 1971 to 2000, which can be associated with its higher TPES share than NG and coal. The global CO$_2$ emission from coal remained consistent from 1985 to 2000, but its CO$_2$ dominance increased from 2005 to 2010. The global CO$_2$ contribution from NG increased 6% from 1971 to 2010.

2.2. Global fossil fuel reserves to production ratio

The biggest concern is how long the global fossil fuel reserves last? The world established oil reserves reached to 1669 thousand million barrels by end-2012. These global oil reserves will be sufficient for 53 years of production and global NG reserves will be adequate to meet 56 years of production with proven NG reserves of 187.3 trillion cubic meters by end-2012. On the contrary, world coal reserves will be sufficient to meet 109 years of global production based on proven reserves of 860.94 billion tonnes by end-2012, which have by far the largest Reserves to Production ratio (R/P) among the fossil fuels. The new and continuing discoveries of oil in South and Central America regions increased global oil R/P by end-2011, whereas single addition of 6.9 billion barrels of oil in official Iraqi reserves increased global oil reserves by end-2012. Similarly, large increase in Turkmen NG reserves increased global NG R/P and reserves in end-2011 [3,23]. The progress in global reserves to production ratio of oil, NG and coal is shown in Fig. 4. The exploited production from coal reserves over the past one decade significantly reduced its R/P. This may be due to increased utilization in coal fired power generation plants for energy production. The development in global proven reserves, production and R/P by three fossil fuels is shown in Fig. 5.

The world liquid fuel comes from crude oil (fields that produce light and medium crude oils), unconventional oil (heavy oils, tars, shale oils, coal to liquids, gas to liquids, and oil or tar sands),
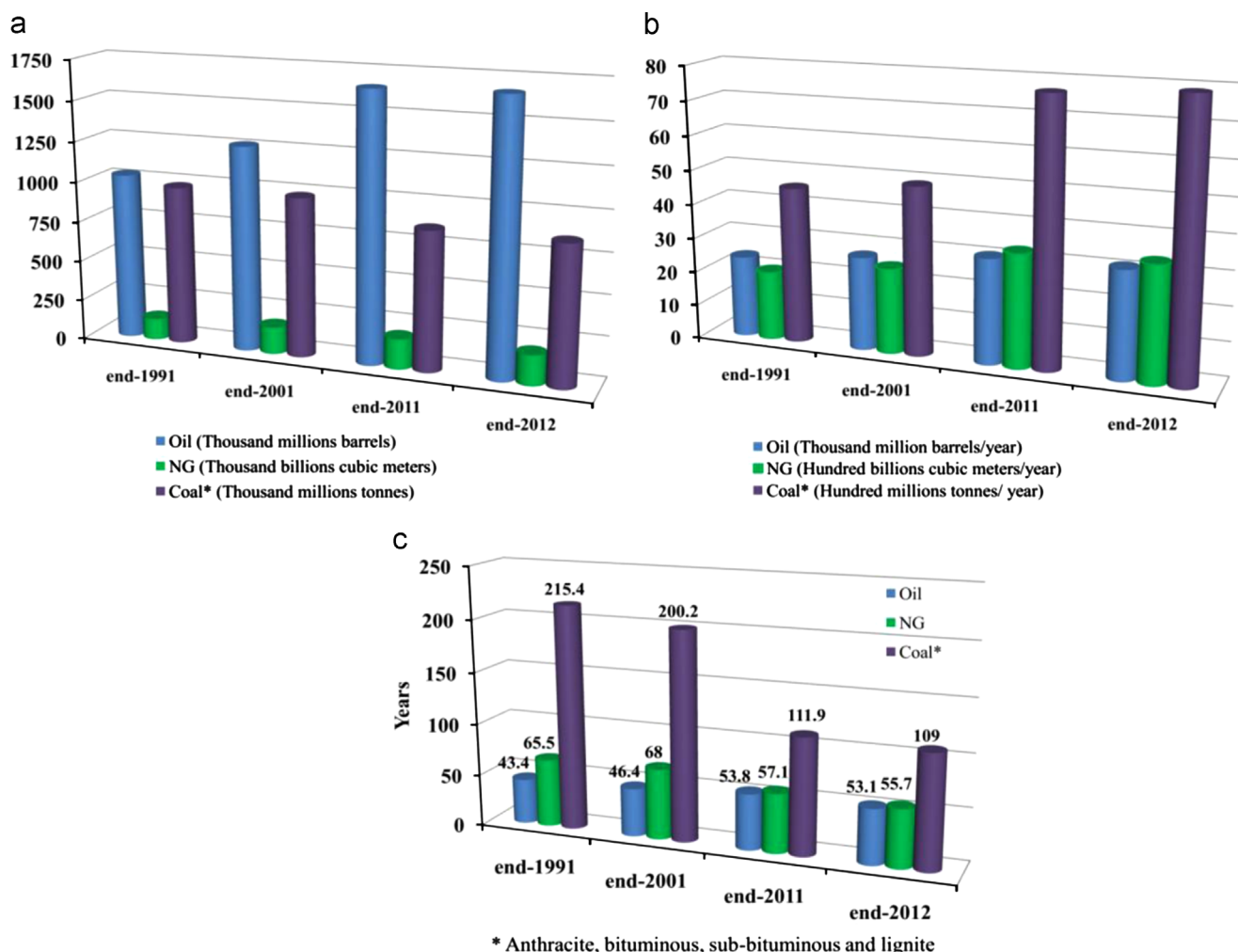

Fig. 5. Development in global oil, natural gas and coal (a) reserves, (b) production and (c) reserves to production ratio (data extracted from [3,24]).

Natural Gas Liquids (NGLs) (the liquefied form of NG), bio-fuels and processing grains. More importantly, world oil production from currently producing fields reached to maximum and oil production rate is expected to decline steadily years after years, if the new crude oil fields were limited and NGLs or unconventional oil production continues insufficiently, a scenario known as peak oil [25,26]. On the contrary, the future energy consumption from NG requires a change in energy sources that is currently satisfied by the liquid fuels and demands more infrastructures in the form of pipeline facilities. However, increased demand of NG in gas exporting countries may contribute to shortage of NG in gas importing countries [27].

The concern over energy insecurity and increased global CO_2 emission from fossil fuel is driving many societies to look for sustainable and clean energy supply. Moreover, global warming resulted from increased dependency on fossil fuel demands mitigation measures, such as a comprehensive switch to sustainable and clean energy sources [28]. The energy insecurity from conventional fossil fuels can be addressed by moderately decreasing dependence on conventional fuels through sustainable utilization of indigenous energy resources and their mix, substituting conventional fuels with coal and renewable biomass sources, such as bio-fuels and waste [29–31]. The most sustainable and considerable alternatives to conventional oil and NG fuels are to explore potential fuels and chemical feedstock from indigenous coal and waste biomass resources [32]. More importantly, oil and NG are considered as one of the quickly depleting natural energy in future. However, substantial contribution of coal, bio-fuels and waste can play vital role to the world energy in future.

3. Coal to liquid fuels

Coal shared 30% to the global energy production with the third highest share after NG and oil in 2009 [15]. More importantly, the global proven coal reserves can provide sufficient amount of energy for the next 109 years, while oil and NG reserves will last for 53 and 56 years of global production, respectively [3]. Based on these facts, coal and coal derived chemicals can play significant role in fulfilling the energy needs of many societies. Moreover, coal may also serve as the most attractive and alternative source for liquid fuels due to the following facts [33]:

- The world coal deposits are estimated higher than other fossil fuels.
- The large recoverable global coal reserves can serve as a supply of synthetic liquid fuels, which can significantly reduce dependence on oil.
- Coal resources are located more widely throughout the world than oil and NG reserves.
- Liquid synthetic fuels from coal would not require comprehensive renewal of present energy infrastructures, e.g. they could flow through existing pipeline networks and can be processed in existing refineries, and petrochemical plants.

Coal To Liquid (CTL) provides one of the more reasonable approach to convert solid coal to liquid fuels and chemical feedstock. CTL technology is based on three fundamental coal liquefaction methods: coal pyrolysis, Direct Coal Liquefaction (DCL) and Indirect Coal Liquefaction (ICL) [34]. Coal pyrolysis refers to thermo-chemical coal conversion in the absence of air or oxygen environment at sufficiently high temperature and low pressure; DCL provides direct coal hydrogenation at high temperature and high pressure; whereas ICL begins with gasifying the coal in the presence of oxygen and steam atmosphere, then converting the syngas (H_2 and CO) to liquid by Fischer–Tropsch synthesis [35].

Coal pyrolysis produces liquid (coal–tar), gas and solid (coal–char). The main chemicals present in the coal liquid are benzene, toluene, xylene, phenolics, naphthalene, anthracene, phenanthrene, pyrene, biphenyl and their derivatives, which can serve as a valuable feedstock for petrochemicals industry [36]. The pyrolysis product yield and composition depend on process temperature, heating rate, rank of coal, reactor design, vapor residence time and inert gas flow rate. Based on these variables, the pyrolysis methods can be sub-divided into slow, flash and fast pyrolysis. The perceived advantages of microwave technology when coupled to fast pyrolysis provide a viable solution for producing liquid and gas fuels from coal. The presence of suitable MWA with coal can convert sufficient amount of MW energy to heat, which can be transmitted to surrounded coal particles provided sufficient penetration depth is maintained, thereby reducing heat transfer problems, which frequently occur in conventional fast pyrolysis systems [9].

4. Biomass to liquid fuels

Biomass To Liquid (BTL) or bio-fuels comprises of liquids and gaseous fuels produced by diverse methods using biomass or waste biomass resources. Bio-fuels can be sub-divided into five main types: (i) biodiesel or bio-alcohols, (ii) vegetable oils, (iii) bio-crude oil or bio-oil or biosynthetic oils, (iv) bio-gas or bio-hydrogen or bio-synthetic gas or bio-syn gas, and (v) Fischer–Tropsch bio-liquids [37]. Bio-fuels and waste contributed approximately 13% to the global TPEC with the highest fuel shares followed by coal, NG and oil in 2010 [15]. The ample quantity of biomass residue generated by processing of various biomasses can be used to recover liquids and chemical feedstock by variety of methods.

The products obtained during thermo-chemical conversion of waste biomass are volatiles (i.e. vapor, gas, and tar components) and solid-char rich in carbon content [38]. Pyrolysis of waste biomass is considered a viable solution for bio-oil and fuel gas production. More importantly, pyrolysis of waste biomass produces energy products with high fuel to feed ratio and broad spectrum of chemicals in bio-oil [39,40]. Besides pyrolysis, fast pyrolysis of waste biomass has attracted great deal of attention for optimizing bio-oil production [37]. The fast pyrolysis bio-oil is a complex mixture of several groups of compounds such as, aldehydes, ketones, sugars, syringols, guaiacols, catechols etc. The main benefit of producing bio-oil using fast pyrolysis is it can be stored and transported to recover valuable chemicals [41]. Despite various improvements in fast pyrolysis systems, it still faces technical issue in improving process energy efficiency, product yield and quality [42,43]. However, MWAP is a promising attempt to resolve these challenges, because of rapid, controlled and efficient heating of materials [44].

5. Microwave energy and dielectric heating

MW falls in between infrared and radio wave regions of electromagnetic spectrum having wavelengths 0.001–1 m with corresponding frequency of 300–0.3 Giga Hertz (GHz). Within this region, frequencies are allocated to cellular phones, radar, and satellite communications. However, in order to avoid interference within the telecommunication devices, Federal Communications Commission regulates the wavelengths for industrial, scientific and medical purpose equipment [45]. For industrial MW processing of various materials, the available frequencies are 0.915 GHz, 2.45 GHz, 5.8 GHz, and 24.124 GHz, while for domestic purpose it is 2.45 GHz [46].

It was often stated that MW can only penetrate to 1–2 cm of materials, which potentially limited its application in diverse fields. However, penetration depth of MW varies with material type, microstructure properties and temperature. For example, water can absorb MW up to 1.4 cm depth at 25 °C and 2.45 GHz, whereas its penetration depth at the same frequency increases to 5.7 cm at 90 °C. In case of quartz glass, the depth is 160 m [47]. The biomass shows variable MW penetration depth depending upon its density and water content. Moreover, the use of 0.915 GHz can provide significantly large penetration depth when compared to 2.45 GHz. These MW frequencies can be preferred in laboratory reactions due to adequate penetration depth under most laboratory operating conditions [48]. The penetration depth is therefore an important parameter in the design of MW cavity size, process scale up and investigation of MW assimilation capacity of materials. The penetration depths of some solid biomass materials are given in Table 1.

The interaction of MW with material can be categorized: (i) insulators, when MW passes through the material without energy losses (i.e. transparent materials), e.g., sulfur; (ii) conductors, MW cannot penetrate through the material and reflect back (i.e. reflector), e.g., copper; and (iii) absorbers, MW is absorbed while passing through material usually called dielectrics e.g., water [46]. Therefore, material can be heated at the expense of MW energy absorption called dielectric heating. The dielectric heating is mainly due to the interaction of electric field component of electrons and charged particles of some materials [52]. The heating mechanism of dielectrics takes place by dipolar and interfacial polarization effects. Considering polar molecules, such as water, the electric field component of MW causes water molecules to rotate and try to align in both permanent and induced dipoles with an alternating field of 2450 million per second, i.e. 2.45 GHz called dipolar polarization. The increased molecular rotation generates friction thereby resulting in heat loss. In the case of dielectric carbon based material having free moving charged particles confined to fixed regions within the material, such as π-electrons, the current travels in phase with the induced electromagnetic field. These π-electrons cannot pair to the phase changes of the electric field; energy is then dissipated in the form of heat called Maxwell–Wagner polarization (interfacial polarization effects) [45,53]. The solid carbon material, which has free moving π-electrons, can be heated by MW energy. The MW interaction with metals or metal powders can also contribute to energy absorption effects [45].

6. Solid microwave absorbers

Most solid materials show relatively low MW absorption when subjected to MW energy. These solid materials cannot be heated to desired temperature using sufficient amount of MW energy. However, dielectrics or MWA are capable of converting good amount of MW energy to thermal energy, which can be transmitted to the supported materials. The MW energy absorption is characterized by dielectric loss tangent parameter, tan δ. The tan δ is the ratio of dielectric loss factor (imaginary permittivity) to dielectric constant (real permittivity). The dielectric loss factor is an important parameter indicating amount of electric energy

Table 1
Penetration depth of materials at various microwave frequencies [49–51].

Material	Microwave frequency (GHz)	Penetration depth (cm)
Oil palm fiber	5.8	10.2[a]
Oil palm shell	5.8	5.5[a]
Biochar	5.8	8.5[a]
Water	2.54	1–4[a], 5–7[b]
Paper, cardboard	2.54	20–60[a]
Wood	2.54	8–350[a]
Natural rubber (caoutchouc)	2.54	15–350[a]
Oil palm fiber	2.54	24.8[a]
Oil palm shell	2.54	13.4[a]
Biochar	2.54	20.6[a]
Oil palm fiber	0.915	67[a]
Oil palm shell	0.915	36[a]
Biochar	0.915	55.6[a]

[a] 25 °C.
[b] 95 °C.

Table 2
Dielectric loss tangent of carbonaceous materials at 2.45 GHz.

Solid carbonaceous materials	tan δ	Ref.
Coal	0.02–0.08[a]	[6]
Carbon foam	0.05–0.20[a]	[59]
Coal char	0.11–0.29[a]	[60]
Carbon black	0.35–0.83[a]	
Activated carbon	0.57–0.80[a]	[61]
Coconut activated carbon	1.65[b]	[62]
Carbon nanotube	0.25–1.14[a]	[63]
CSi nanotube	0.58–1.00[a]	[64]
Wet empty fruit bunch char	0.31[b]	[62]
Dried empty fruit bunch char	0.34[b]	
Oil palm shell activated carbon	0.40[b]	
Dried oil palm empty fruit bunch char	0.13[b]	
Empty fruit bunch sample with 18, 45 and 64 wt% moisture	0.30[b], 0.54[b], 0.32[b]	
Oil palm fiber	0.08	[49]
Oil palm shell	0.12	
Oil palm shell char	0.08	
Wood	0.11	[50]
Fir plywood	0.01–0.05	
Particle board	0.1–1.0	
Aspen bark	0.22	
Pine bark	0.18	

[a] 25 °C.
[b] 27 °C.

dissipated in the form of heat within the material, whereas dielectric constant specifies the amount of electromagnetic incident energy reflected and absorbed by the material [53]. The loss tangent parameter is therefore helpful in studying the MWH processes. Various solid materials behave differently when subjected to MW energy.

6.1. Solid carbonaceous microwave absorbers

Solid Carbon Based Materials (SCBMs), in general, are good MWA. More importantly, SCBMs can indirectly heat materials which are relatively transparent to MW. Different carbon based materials have been applied as a MWA in various Microwave Heating (MWH) processes, such as sewage sludge [54], biomass pyrolysis [55–57], catalytic heterogeneous reactions [58] etc. The dielectric loss tangent (tan δ) of some carbonaceous materials is listed in Table 2. It can be seen that the loss tangent of most carbon based materials is higher than coal and waste biomass. The addition of higher dielectric loss material with coal and waste biomass can provide some perceived benefits: (i) increases MW assimilation capacity of bulk material, (ii) transmits heat to the surrounding material, and (iii) provides sufficient temperature at low MW power.

Another interesting feature of SCBMs when heated by MW energy is that it can give rise to hot spots that appears as small sparks or electric arcs termed as micro-plasmas. The appearance of micro-plasmas is limited to tiny space and lasts only for fractional second [65]. Micro-plasmas are of two types depending on shape and nature: ball lighting and arc discharge effects. Ball lighting is the formations of quasi-spherical plasmas and their appearance can be observed during MWH of SCBMs regardless of the material temperature. On the other hand, electric arcs are more abundant at relatively higher temperatures [66–68]. These hotspots (micro-plasma) are created due to non-linear supply of MW and variations in thermo-chemical properties of dielectric and heating material in Multimode Microwave (MMW) system [69]. Therefore, MWH of material with SCBMs may result in thermal instability and localized heating of materials. Jones et al. [70] reported that hotspots may occur due to two reasons: (i) the standing MW within the MW cavity may result in increased heating in some regions exposed to higher energy than the others and (ii) non-uniform mixing of MWA with low loss dielectric materials. However, it was suggested that the good cavity design can minimize and control hotspots. Several techniques have been suggested to overcome hotspots in MMW by increasing the size of the MW cavity, increasing MW frequency, rotating the material, and using

multiple MW inputs [71]. However, most studies focused toward intimately mixing of MWA with material promoting localized heating and uneven heating rate. The choice and distribution of MWA with pyrolytic material can play a vital role to reduce hotspots.

6.2. Metal oxide microwave absorbers

Coal and waste biomass show relatively low MW absorption capacity, although moisture and some mineral matter within the coal and waste biomass quickly respond to MW energy [6,67,72]. Metallic oxides can serve as better MWA, which can provide several benefits: effectively absorb MW energy, increase the heating rate of materials, and facilitate de-volatilization from coal and waste biomass. The evolved vapor and gas can be simultaneously cracked and catalyzed while contacting heated metallic coal–char or bio-char. In addition, metal oxides MWA can influence product yield and quality during MWAP of coal and biomass [9,73].

7. Microwave and conventional pyrolysis of coal and waste biomass of isolated fuel

MW provides a unique method of transferring energy from source to the material compared to conventional heating. Conventional heat is transferred to the center of material by conduction and convention only. On the contrary, MWH is characterized by the transfer of electromagnetic energy to thermal energy. The opposite temperature gradient is established in both heating systems since during MWH material is at a much higher temperature than its surrounding, unlike conventional heating where it is necessary for the conventional furnace cavity to reach the operating temperature and begin heating the material [74]. As a result of heating, both systems show different temperature distributions as illustrated in Fig. 6.

More importantly, the solid phase reactions, de-volatilization or heterogeneous reactions are favorable in MWH while homogenous gas-phase reaction improves in conventional heating. Additionally, lower temperatures in MW cavity can be useful to avoid undesirable reactions in vapor and gas phase species. Longer heating period, opposite thermal gradient, and energy lost to the environment in conventional heating can be avoided during MWH. Furthermore, improved volumetric heating of materials can be achieved due to sufficient penetrating capacity of MW. These qualities make MWH an attractive and alternative to conventional heating methods [74].
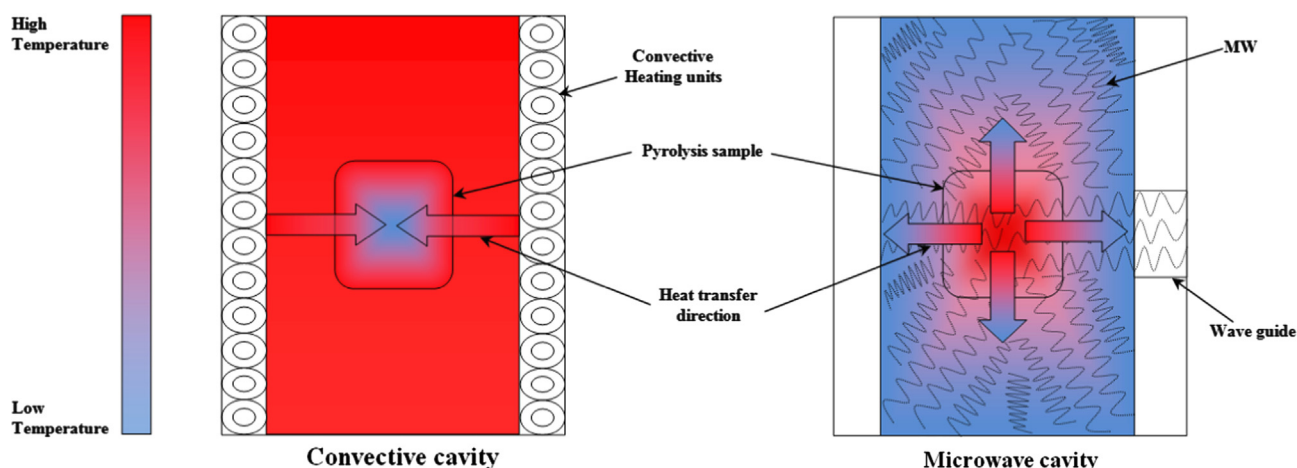

Fig. 6. Temperature distribution and direction of heat transfer in pyrolysis systems.

Gasner et al. [12] compared the product distribution of coal in MWAP and CPS. The MWAP of coal in the presence of copper wire achieved quick release of volatiles and improved coal–tar yield from MW plasma pyrolysis indicating that copper wire produced much higher temperature and acted as MW antenna. The study espoused that conversion of gas and volatiles from MW plasma pyrolysis of coal can be achieved at much shorter duration and residence time compared to MW arcing and muffle furnace. The MWAP of coal in the presence of copper-wire improved coal–tar yield to 14 wt% compared to only 1 wt% using the conventional method. However, gas yield from muffle furnace was found higher than MW plasma procedure, but gas composition from both systems was found similar. The study, however, did not report temperature profile and final temperature reached in both heating systems. Despite the improved coal–tar yield from MW plasma pyrolysis of coal, this area of coal pyrolysis has not been investigated in detail. This may be due to intense plasma formation, significant high temperature and difficulty in measuring temperature.

In another study [8], low ranked coal was subjected to MWAP and CPS. Coal–char was added as a MWA to increase MW assimilation capacity of coal at three MW power levels, which raised coal bed temperature to 800 °C within 5 min. Whereas, electric tube furnace produced similar temperature consuming 35 min at much lower heating rate. The coal–tar yield and weight loss proportion from MWAP were found higher than CPS, which was reported by the difference in heating rate and secondary vapor-phase reactions such as, condensation and polymerization. Moreover, cumulative share of syngas was found much higher under MW operating conditions, which was related to the temperature distribution. The difference in product profile and composition from MWAP and CPS of coal is mainly due to the presence of high dielectric loss material in MWAP, which primarily limits its direct comparison to CPS since no such material is added in CPS to absorb heat at much faster rate.

Dominguez et al. [75] employed electrical furnace and MMW to characterize and compare pyrolysis products of coffee hull pellets. The MWAP in the presence of char (a MWA) at an average MW power of 130 W, 270 W and 420 W raised biomass temperature to 500, 800 and 1000 °C, receptively within 5 min. Whereas, electric furnace attained comparable conditions after 10 min using similar coffee hull pellets to char ratio, which were employed during MWAP. Interestingly, results indicated that MWAP produced more gas and less oil than CPS under comparable condition. The H_2 and syngas gas contents from MWAP were reported much higher than CPS. This improved syngas yield was ascribed mainly due to the

presence of char additive with biomass pellets. It was suggested that an increase in the total amount of char (i.e. added as a MWA and formed during pyrolysis of biomass pellets) can improve heterogeneous gas-phase reactions. Moreover, the MWAP char showed much higher porosity than CPS char, which was supposed to play an important role in char self-gasification reactions. Furthermore, the addition of char to coffee hull in CPS appears to contribute towards increased oil yield. However, the exact reason behind increased oil yield from CPS is still lacking in this study.

Wang et al. [72] compared gas and char production from MWAP and CPS of pine sawdust. A specially designed three wave generator at 2000 W and 2.54 GHz was used to control final pyrolysis tempertaure. The addition of charcoal (MWA) outside the sample curcible was ensured to achieve complete inert pyrolysis conditions. The study adopted a unique fast MWAP approach by preheating MW system in the presence of charcoal to reach pyrolysis temperature and then dropping the pine sawdust sample into the crucible. This resulted in very fast MWAP pyrolysis and produced less char and high syngas yield compared to CPS. Moreover, bio-char was less reactive towards gas during MWAP exceeding 600 °C, which was assigned to char meltdown, shrinkage of pores size and decrease in specific surface area of bio-char. Fernández and Menéndez [56] utilized sewage sludge, coffee hulls and glycerol to compare variation in feed characteristics on pyrolysis yield and gas compositions from MWAP and CPS. It was concluded that MWAP always results in increased gas yield with high syngas content than CPS. It was also espoused that MWAP produce desired effect with incerased temperature due to the hotspot phenomenon, which only occurs in MWH.

Zhao et al. [14] applied 18,000 W MW power to pyrolyze wheat and corn straws without MWA and achieved maxium pyrolysis temperature of 600 °C. The liquid, gas and solid yields of using wheat and corn straws were reported close to 1:1:1 under most MWAP operating conditions. It was determined that the MWAP of biomass provides higher heating rate and more valuable pyrolysis products compared to CPS. Moreover, the total syngas volume under MWAP environment was reported higher than CPS. The comparison of product yield and gas fractions from MWAP and CPS of coal and biomass resources is presented in Table 3.

The difference in pyrolysis product and composition from MWAP and CPS can be explained in terms of differential heating mechanism in two systems. In CPS, heat is transferred to the solid biomass particles by thermal means, which mainly depends on its thermal conductivity. However, most biomass solids demonstrate

Table 3
Product distribution from microwave and conventional pyrolysis of coal and biomass.

Feed stock	Product yield and composition	Microwave pyrolysis	Conventional pyrolysis	Ref.
Coffee hull pellets	Oil yield (wt%)[a]	9.80–13.57	7.90–9.19	[75]
Pine sawdust	H_2 vol%[b]	16–32	0–22	[72]
	CO vol%[b]	41–48	33–50	
	CO_2 vol%[b]	6–28	10–53	
Coffee hull	Gas yield (wt%)[c]	60–75	55–65	[56]
	Syn gas (H_2+CO) L/g of biomass feed	0.41–0.62	0.17–0.36	
	CO_2 production	0.20–0.34	0.45–0.65	
Wheat straw bales	Syn gas (H_2+CO) vol%[d]	54% of total gas volume (37% H_2)	< 40% of the total gas volume	[14]
Corn straw bales		54% total gas volume (35% H_2)	< 40% of the total gas volume	
Bituminous coal	Oil yield (wt%)[e]	14	1	[12]
	Gas yield (wt%)[e]	17	30	
Low rank coal	Gas yield (wt%)[f]	11.8[g]	6.80[h]	[8]
	Syn gas (H_2+CO) vol%[f]	Up to 55	Up to 42	
	CO_2 vol%	3.61–4.01[i]	4.20–5.41[j]	

na—not available; [a] temperature 500–1000 °C, MW power 130–420 W, MWA char; [b] temperature 400–800°C, MW power 2000 W with temperature control, MWA charcoal; [c] temperature 400–900 °C, MW power na, MWA na; [d] temperature na, MW power 18,000 W, MWA na; [e] temperature 750 °C, MW power na, MWA copper wires; [f] MW power 616 W, MWA na; [g] temperature 616 °C; [h] temperature 600 ºC; [i] temperature 440–800 ºC; [j] temperature 600–800 ºC.

low thermal conductivity [76] and heated in convective cavity environment by conduction and convection only. The solid particles near the convective heated cavity quickly attain pyrolysis conditions than the solids next to or in the middle of the material. This heating strategy can result in slow and differential heating of bulk biomass solids. On the contrary, MWAP of biomass offers internal and volumetric heating of bulk biomass solids due to the strong interaction of MW energy with the biomass moisture at molecular levels [77]. This selective heating nature of MW vaporizes the moisture within the depth of biomass particles and generates steam, which can increase the temperature of bulk biomass solids [55]. In addition, the heated steam favors low temperature volatile sweeping and forms several channels within the biomass to increase its porosity [78]. Several authors reported low temperature MWAP of biomass [79–82].

Solid carbons are usually added to coal and biomass to improve process heating rate under MW pyrolysis conditions [7,83–86]. This improved heating rate is mainly due to the fact that MW energy directly interacts with the solid carbons and heated to higher temperature than the surrounding coal and biomass particles. The pre-heated carbons then transmit heat to the nearby particles, which quickly achieve pyrolysis conditions. This improved heating strategy in the presence of solid carbon favors rapid de-volatilization of coal and biomass particles. Moreover, the evolved vapors flow through a fairly low temperature MW cavity environment, which reduces the chances of secondary vapor-phase reactions. More importantly, the volatile-carbon interaction is supposed to play an important role in improving the vapor-phase selectivity. As discussed earlier, the presence of carbons with pyrolysis material commonly produces micro-plasmas under MW irradiation conditions. These micro-plasmas or electric arcs are believed to be at much higher temperature than the bulk material, which can favor heterogeneous gas-phase reactions. The heterogeneous gas-phase reactions over solid carbon surface have been found effective under MW irradiation conditions, such as catalytic CH_4 decomposition to produce H_2 over activated carbon ($CH_4 \rightarrow C + 2H_2$) [87,88], dry CO_2 and CH_4 reforming over activated carbon ($CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$) [89,90], NO_x reduction over sub-bituminous coal–char, anthracite and metallurgical coke ($C + 2NO \rightarrow CO_2 + N_2$ and $C + NO \rightarrow CO + \frac{1}{2}N_2$) [91,92] and SO_x reduction over sub-bituminous coal–char and anthracite ($C + SO_2 \rightarrow CO_2 + S$ and $2C + SO_2 \rightarrow 2CO + S$) [93]. Based on these facts, it can be rationalized that the MWAP of coal and biomass in the presence of carbon particles (a MWA and catalytic precursor) always results in better pyrolysis products.

8. Microwave assisted pyrolysis of coal

The nature of coal decomposition depends on the reaction temperature, mode of heating and heating rate. The use of various energy sources, e.g. plasmas jets, high intensity d.c. arc, laser beam, flash heating and arc imaging reactors, has shown extremely rapid pyrolysis of coal and produced high yields of acetylene. However, these studies of coal pyrolysis using various energy sources have focused toward coal gasification [94–97]. Moreover, the solar irradiation can also be used to de-volatize the coal [98]. MWH has been used in coal science and technology due to its increased attention and prospect, such as drying, grinding, gasification, desulfurization and pyrolysis [9,99–103]. Moreover, it has been applied to coal liquefaction with various liquid solvents [103,104]. In this concern, the use of MWH during fast pyrolysis of coal can serve as exploring the potential of liquid and gas fuels.

Coal is essentially transparent to MW energy due to fairy low dielectric loss tangent value. This low dielectric value of coal signifies the major stumbling block during MWAP [6], although moisture and some minerals, such as pyrite and other metallic

minerals within the coal matrix, respond more readily to MW due to their high dielectric loss value [67,105,106]. Moreover, the coal sample cannot be pyrolyzed or reach sufficient temperature without MWA even with high MW power source [105]. However, metallic oxides and metal can quickly raise coal bed temperature to initiate de-volatization during MWH [9,10,12].

8.1. Microwave assisted pyrolysis of coal with solid carbonaceous absorbers

Solid carbonaceous MWA has been used to increase MW assimilation capacity of coal. Cha et al. [83] observed that the addition of coal–char (MWA) with coal can increase reaction rate and reduce activation energy during MWAP when compared to CPS. It was suggested that, coal–char can serve as a better MWA and enhance coal reactions in MWH by (i) the elements in coal molecule which may react directly with coal–char, (ii) increase the amount of free radicals formation due to sufficient coal–char interaction, and (iii) increase the heat transfer from coal–char to surrounding coal particles.

Liu et al. [7] studied heating rate of coal without and with four solid carbonaceous MWA (activated carbon, 550-carbocoal, 650-carbocoal and 750-carbocoal) during MWAP. The carbocoals were produced from coal in conventional furnace environment at 550, 650 and 750 °C. The use of coal alone at 700 W was reported to achieve a temperature of 300 °C in 30 min. However, 650-carbocoal, 750-carbocoal and Activated Carbon (AC) with coal at 700 W showed high heating rate and attained 700 °C in less than 2 min, but 550-carbocoal showed significant decrease in heating rate. The high heating rate of AC was assigned to its high dielectric loss parameter, whereas differences in heating rate among carbocoals were attributed to variation in their microstructures formation during CPS. The use of 750-carbocoal with coal of 2:5 produced maximum coal–tar yield of 12.01 wt%. However, increasing ratio of 750-carbocoal to coal beyond 2:5 decreased liquid yield due to increased heating rate and secondary cracking of vapors. The product distribution and composition of coal from 550-carbocoal, 650-carbocal and AC are still lacking in this study. In another study [8], the addition of coal–char to coal at three MW powers of 440 W, 616 W and 800 W raised the coal bed temperature to 800 °C within few minutes. However, increased power showed some variations in heating rate, product yield and composition. In addition, it was espoused that optimum coal–char to coal ratio can serve as controlled heating rate, which can improve liquid and gas yields. Unfortunately, the variation in heating rate at three MW power levels and the coal–char to coal ratio are still lacking in the study.

8.2. Microwave assisted pyrolysis of coal with metal oxide absorbers

The absorption of electromagnetic energy depends on coal type and its mineral matter. Coal is also composed of minor inorganic species, which quickly respond to MW. Metallic substances can be used to increase MW assimilation capacity of coal. Certain metal oxides are capable of strong MW energy absorption [107,108]. Among several metallic oxides, Fe_3O_4 and Fe_2O_3 have the ability to strongly interact with MW energy [107]. Ma et al. [109] reported that the strong coupling of Fe_3O_4 with MW energy can be explained by the ferromagnetic property and magnetic losses may be responsible for triggering the temperature during MWH. In the case of non-ferromagnetic materials, the rapid heating and interaction may be due to electromagnetic nature of MW and material. Beside Fe_3O_4, CuO is one of the transition metal oxides that best couples to MW and can increase temperature within few minutes [110]. The behavior of transition metal oxides during MWH has been studied extensively [108,111–113]. Transition metal oxides, such as CuO, Fe_3O_4, MnO_2, CoO, Co_3O_4, NiO, CuO, and Ag_2O, are good MWA at room temperature [110]. Xu and Tomita [114] reported that certain metallic oxides have the ability

to crack aliphatic and aromatic hydrocarbons during coal pyrolysis and are found to be in the order of $Fe_3O_4 > Al_2O_3 > CaO > SiO_2 >$ quartz bead.

Monsef-Mirzai et al. [10] used inorganic receptors to investigate the effects of coal pyrolysis during MWH. The use of CuO showed relatively high MW assimilation capacity and raised coal bed temperature to 700 °C within few minutes. Moreover, the study suggested that MWH of some metal oxides increased the coal temperature without the initiation of plasma formation. This perceived benefit of metal oxides can be utilized to simultaneously heat all coal particles in the absence of plasma formation.

Later, Monsef-Mirzai et al. [9] used CuO, Fe_3O_4 and metallurgical coke to pyrolyze coal at 650 W and 2.54 GHz. The two metal oxides raised the coal bed temperature to 1200–1300 °C within 3 min. This sufficiently high temperature was found by using non-stoichiometric amount of MWA with coal (i.e. 3 g of each CuO, Fe_3O_4 and metallurgical coke was intimately mixed with 0.5 g coal). Moreover, the use of nitrogen gas from reactor bottom resulted in fairly high coal–tar yield using CuO compared to Fe_3O_4 and metallurgical coke, but CuO assisted coal–tar always contained soot which remained a problem. This increased soot formation was ascribed to increase secondary cracking of coal vapors and non-stoichiometric amount of CuO. However, the use of Fe_3O_4 enhanced syngas $(CO+H_2)$ yield to 65.47 vol% compared to 15.77 vol% using coke, but H_2 gas predominated the entire gas phase. The study also revealed that mineral sulfur within coal was found immobilized using CuO and coal–char showed a high degree of graphitization, which can be reused as MWA. More importantly, the study investigated maximum temperature attained using various arrangements of metal oxides with coal and coke. The use of single thick layer of CuO over coal in a ratio of 6:1 resulted in uneven heating rate and plasma formation from CuO surface. However, intimately mixing of CuO and coal covered with coke layer achieved smooth heating rate, but sufficient data is lacking of coal–tar yield and composition using layered method. The study also reported that CuO produced excellent coal–tar yield of 49 wt% in some cases, which was referred to the previous work [10]. Unfortunately, sufficient data of CuO based coal–tar yield and composition is lacking to produce more details.

8.3. Microwave assisted pyrolysis of coal with metals

In a novel method of coal pyrolysis in MWH, Gasner et al. [12] espoused that the coal pyrolysis in the presence of copper wires produced plasma initiation procedure. This method caused rapid coal de-volatization, which increased system pressure. However, it was suggested that without any plasmas initiation, the system pressure remained very low over the reaction period. Moreover, the use of copper metal wires produced 14 wt% coal–tar, which was significantly higher than muffle furnace under comparable conditions. The coal–tar was composed of heavier hydrocarbons. The study suggested that coal–char formed during metal assisted pyrolysis was found porous and showed no evidence of deformation, which can be used as feedstock either in fluidized bed combustion or gasification. In another similar study [11], various shapes of iron metal were applied to pyrolyze coal during MWH. The use of iron metal induced severe cracking of coal and raised coal temperature to 1000–1200 °C. However, volatiles formed during coal pyrolysis stick inside the condenser tubes and was found soluble in hot coal–tar. The amount of oily and sticky liquid, and coal conversion, was found dependent on shapes of iron metals used. However, iron mesh coil resulted in higher coal–tar yield compared to solid iron cylinder and iron strips, but liquid contains variety of aromatic and aliphatic hydrocarbons. The product distribution from MWAP of coal with metallic oxides and metals is shown in Table 4 and is compared with carbonaceous MWA.

9. Microwave assisted pyrolysis of waste biomass

Waste biomass is composed of organic and inorganic species in varying quantity. Waste biomass shows some improved MW absorption capacity due to the presence of relatively high moisture and inorganic substances. MWAP of waste biomass without MWA requires considerable power to reach pyrolysis temperature. On the contrary, the use of MWA can improve pyrolysis temperature at significantly low MW power. Moreover, inorganic additives with waste biomass can serve as MWA and participate in improving selective compounds in bio-oil. MWAP of waste biomass has attracted great deal of attention for optimizing liquid yield. Bridgwater and Peacocke [41], and Vamvuka [115] reported that MWAP of biomass can improve bio-oil yield and process energy efficiency under various operating conditions. The MWAP of waste biomass resources has been investigated extensively without MWA, with MWA and inorganic additives.

9.1. Microwave assisted pyrolysis of waste biomass without microwave absorber

The MWAP of pelletized wheat straw in the absence of MWA requires sufficiently high MW power of 1000–2000 W [13]. Miura et al. [78] carried out MWAP of four larch cylindrical wood samples of different weights and sizes (80, 190, 370, 12,000 g with 60, 80, 100 and 300 mm diameter, respectively) using fixed power

Table 4
Product distribution from microwave pyrolysis of coal with metal oxides, metals and carbonaceous microwave absorbers.

Heating system	MW receptor	Yield wt%			Reference
		Oil	Gas	Char	
Microwave[a]	Copper wires	14	17	69	[12]
Microwave[b]	Iron mesh	28	22	25	[11]
	Iron coils	39	20	16	
	Iron solid cylinders	23	23	30	
	Iron strips	28	22	25	[9,10]
Microwave[c]	CuO	Max. 49	na	na	
	Metallurgical coke	Max. 20[d]	na	na	
	Fe_3O_4	Max. 27[e]	na	na	
Microwave[f]	750-carbocoal	Max. 12.01[g]	Max. 14.32[h]	Max. 66.81[g]	[7]
Microwave	Coal–char	Max. 9.60[i]	Max. 11.8[i]	Min. 78.60[i]	[8]

na—not available; [a] coal size 6–12 mm, 650 W vacuum pressure 2 torr, 15 min.; [b] coal size na, MW power na, temperature 1000–1200 °C, time na, aqueous liquid in all four metal shapes 25 wt%; [c] coal size 90–212 μm, 650 W, 3 min.; [d] same as [c] but max. temperature 1312 °C, Coke (3 g) to Coal (0.5 g); [e] same as [c] but max. temperature 1188 °C, Fe_3O_4 (3 g) to Coal (0.5 g); [f] coal size < 1 mm, 1–3 mm, 3–6 mm, 700 W, 15 min., max. temperature 750 °C; [g] same as [f], but 750-receptor to coal ratio 2/5; [h] same as [f] but 750-receptor to coal ratio 3/5; [i] coal size < 5 mm, 440 W, 30 min., max. temperature 700 °C, receptor to coal ratio na.

Table 5
Product distribution from microwave pyrolysis of waste biomass without and with solid carbonaceous microwave absorber.

Feedstock	Operating conditions	Bio-oil yield (wt%)	Bio-oil composition (% area of GC–MS)	Gas yield (wt%)	Gas composition (vol% of the total gas)	Ref.
Without microwave absorber						
Wheat straw pellet (cylindrical shape) 1×1 cm^2	Sweeping gas helium, 1000–2000 W, 1–5 min	27.90	Phenols, guaiacols, cresols, condensed aromatics	46.10	H_2=1.3, CO=24.4, CO_2=14.5, CH_4=2.6, C_2H_2=1.2, C_2H_4=1.5, C_2H_6=0.6, Others=53.9	[13]
Larch samples of diameter 60, 80, 100 and 300 mm, weight 80, 190, 370 and 12,000 g respectively	Sweeping gas N_2, variable power 100–1500 W, 3–18 min	26.4[a]	Carboxylic acids, furfural, cresol, guaiacol, eugenol, arabinoses, xylitol, levoglucosan, etc.	na	na	[78]
Rice straws	Sweeping gas N_2 50 mL/min, reaction time 30 min, 50–500 W, Max. temperature 105–563 °C	Max. 22.56[b]	Alkanes=43.68, polars=25.84, polycyclic aromatic hydrocarbons =8.94, others=21.54	Max. 49.37[c]	H_2=55, CO=13, CO_2=17, CH_4=10, Others=5	[117]
Rice straws	Sweeping gas N_2 50 mL/min, 200–500 W, 260–500 °C	na	na	na	(At 300 W and max. 400 °C) H_2=50.67, CO_2=22.56, CO=10.09, CH_4=7.42, Others=9.26	[57]
Wheat straw pellets	Vacuumed, heating rate with additives 17 °C/min, 1000 W[a] (Max. 1200 W), 130[a]–180 °C[f], time 130–165 min, pre-treatment of feedstock with additives (H_2SO_4, HCl and NH_3)	Max. 22.1[d]	1,4:3,6-Dianhydro-α-D-glucopyranose=1.27[e]–6.69[g], levoglucosan=27.87[e]–46.44[h], levoglucosenone=1.51[d]–23.63[g], phenols=15.85[h]–20[e], desaspidinol=1.3[e]–2.74[h]	Max. 20[h]	na	[79]
Corn stover, air dried, particle size 0.5–4 mm	Sweeping gas N_2, 700 W, reaction temperatures 515–685 °C, reaction time 4–22 min	Max. 36.98[i]	Phenols=28–40, aliphatic hydrocarbons=11–24, aromatic hydrocarbons, furan derivatives, some acids, etc.	Max. 42.36[j]	na	[116]
Rice straws	Sweeping gas N_2 50 mL/min, reaction time 30 min, 50–500 W	na	–	40	H_2=50.67, CO=16.09, CO_2=22.56, CH_4=7.4, Others=3.26	[57]
Wheat straws and corn straws bales $1 \times 0.6 \times 0.6$ m^3	Sweeping gas N_2, reaction time 85 min, 18,000 W, max. temperature 600 °C	Approx. 33.30[k]	na	Aprox. 33.30[k]	H_2=36, CO=18, CO_2=19, CH_4=22, Others=5	[14]
With carbonaceous microwave absorbers						
Cylindrical coffee hulls pellets (3 mm dia. × 2 cm length)	Fixed amount of bio-char, N_2 at 60 ml/min, reaction time 15 min, 130–420 W, 500–1000 °C, single mode microwave	7.90[a]–9.19[b]	na	68.72[c]	H_2=40.06[c], CO=32.75[c], CH_4=6.74[c], CO_2=17.73[c], C_2H_4=2.15[c], C_2H_6=0.56[c]	[75]
Oil palm fiber, oil palm shells (OPF 300–600 μm and OPS 0.001–0.002 m)	OPF and OPS to bio-char ratio (1:0.25, 1:0.50 and 1:0.75), N_2 at 10 ml/min, reaction time 25 min, fluidized MW heating, 450 W	Max. 22[d], Max. 25[e]	Ketones, aldehydes, carboxylic acids, nitrogenous compounds, alcohols, esters, ethers etc.	Max. 29[d], Max. 30[e]	na	[119]
Oil palm shells (OPS-850 μm)	OPS to CAC ratio (1:0.25, 1:0.50 and 1:0.75), N_2 at 5 ml/min, reaction time 25 min, over head stirred fluidized MW heating, 300 W and 450 W, fixed stirrer speed 200 rpm	Max. 17[f]	(At 450 W, 50% CAC) Phenol=72.1, o-cresol=3, p-cresol=2.4, 2-methoxy-4-methyl-phenol=5, 2-Methoxy-phenol=9, 4-Ethyl-2-methoxy-phenol=4.4, 2,6-Dimethoxy-phenol=3.9, Others=not detected	Max. 47[g]	na	[55]
Empty fruit bunch pellets (0.4–4 cm long having diameter 0.7 cm)	EFB pellets to CAC ratio (1:0.25, 1:0.50 and 1:0.75), N_2 at 4 ml/min, reaction time 25 min fluidized MW heating, 300 W and 450 W	Max. 22[g]	(At 450W, 75% CAC) o-cresol=6.1, p-cresol=5.3, 2-methoxy-phenol=26, 2-methoxy-4-methyl-phenol=9.8, 4-ethyl-2-methoxy-phenol=10.5, 2,6-dimethoxy-phenol=14.3, 1-(2,6-dihydroxy-4-methoxyphenyl)-ethanone=4.1	Max. 31[g]	na	[120]
Oil palm shell (1.4 mm)	OPS to CAC ratio (1:0.25, 1:0.50 and 1:0.75), N_2 at 7 ml/min, reaction time 30 min, over head	Max. 27.5[h]	(At 450 W, 75% CAC, 100 rpm) Phenol=84.7, 2-methoxy-phenol=6.7, 2-methoxy-4-methyl-phenol=2.1	Max. 47[i]	na	[121]

Table 5 (continued)

Feedstock	Operating conditions	Bio-oil yield (wt%)	Bio-oil composition (% area of GC-MS)	Gas yield (wt%)	Gas composition (vol% of the total gas)	Ref.
Pelletized douglas fir 0.7 cm in diameter and 1.5 cm in length	stirred at 50, 100 and 150 rpm, 450 W Douglas fir to activate carbon ratio (1.32:1–4.86:1), 700 W, temperature 350–484 °C, time 1.27–15 min	6.8^j–48.1^k	Phenolic compounds=66.9 including 38.9% area of phenol	13.1^l–66.2^m	na	[122]
Wheat straw of size <0.09 mm	Wheat straw to pyrolysis residue 2:1, N_2 at 5–30 ml/min, reaction time 10 min, 900 W, max. temperature 1000 °C using 200 °C hot air	25–31^n	na	18–22^n	H_2=22.1–43.7^n, CO=34.7^n, CO_2=23.6–33.8^n, CH_4=7.9^n	[123]
Douglas fir sawdust pellet (0.7 cm diameter and 1.5 cm length)	Four acid washed activated carbons (coconut shell based, wood based, bituminous coal based and lignite based), DF sawdust pellets to four AC ratios 1:3, N_2 flow rate na, 700 W, 8 min	26.5^p, 28.9^r, 31^q, 33.2^s, 45.2^s	Phenols=2.54^s–74.77^r, guaiacols=1.33^p–48.78^s, furans=3.9^s–14.24^q, ketones/aldehydes=2.02^r–16.85^q	11.8^s, 44.6^q, 44.8^o, 47.53^r, 52.67^p	na	[125]

Without microwave absorber, na—not available; [a] 100 mm dia, 0.351 kg, 7 min.; [b] 20/40 mesh size, 407 °C, 300 W; [c] 20/40 mesh size, 407 °C, 300W; [d] with HCl (3% v/v); [e] without additive; [f] with additive; [g] with H_2SO_4 (10% w/w); [h] with NH_3 (3% v/v); [i] 1mm particle size, 650 °C, 18 min; [j] 3 mm particle size, 650 °C, 8 min; [j] based on 1:1:1 of liquid: gases: solids.

With carbonaceous microwave absorbers, na—not available; [a] 500 °C, 130 W, 15 min.; [b] 800 °C, 270 W, 15 min.; [c] 1000 °C, 420 W, 15 min.; [d] OPF to bio-char ratio 1:0.5, 450W, 25 min; [e] OPS to bio-char ratio 1:0.5, 450 W, 25 min; [f] OPS to CAC ratio 1:0.5, 450 W; [g] OPS to CAC ratio 1:0.25; [h] same as [f] with 100 rpm; [i] same as [g] with 50 rpm; [j] same as [g] with 50 ppm; [k] 350 °C, 12 min, Douglas fir to activated carbon ratio 2:1; [l] 400 °C, 15min., no activated carbon; [m] 350 °C, 12 min, Douglas fir to activated carbon ratio 4:1; [n] 400–600 °C; [o] coconut shell based; [p] wood based; [q] bituminous based; [r] lignite based; [s] no activated carbon.

of 1500 W for more than an hour, which resulted in bio-oil yield of 10.8–31.5 wt%. This bio-oil contained 5–8.8 wt% levoglucosan under various MW operating parameters. It was suggested that short volatiles residence time in MW reaction zone by using high inert gas flow rate can contribute to increased levoglucosan yield and reduce the chance of volatiles sticking on the reactor wall. In another study [79], pre-treated wheat straw pellets with H_2SO_4, HCl and NH_3 were subjected to MW pyrolysis. The pellets rose to 180 °C using 1200 W. However, the resulted bio-oil showed some improved chemical profile compared to untreated bio-oils. The bales of wheat and corn straws reached a temperature of 600 °C at 18,000 W; however, liquid, gas and solid yield remained close to 1:1:1 under most operating conditions [14]. MWAP of corn stover at 700 W and 4–22 min resulted in 37 wt% bio-oil and 42 wt% gas at temperature of 515–685 °C. Moreover, the effect of particle size was reported insignificant and very fine feedstock grinding is not necessarily required, which can result in substantial energy savings [116].

Huang et al. [117] applied single mode MW power 50–500 W to rice straw particles. With 300 W, heating rate of 55 °C/min at 407 °C resulted in maximum bio-oil of 22.56 wt% and 49.37 wt% gases. However, 400–500 W power and particle size were reported to affect MWAP performance. The syngas was reported to 68 vol% (with 55 vol% H_2 of total gas) and bio-oil contained alkanes, polars and low-ring polycyclic aromatic hydrocarbons suggesting enhanced recovery from waste biomass. Later, Huang et al. [57] produced high content H_2 gas of 50.67 vol% from MWAP of rice straw and espoused that approximately 60% of MW energy input can be utilized effectively to derive as useful bio-energy. The product distribution and composition from MWAP of waste biomass resources without MWA are summarized in Table 5. It can be analyzed that the product yield requires considerable MW power to pyrolyze waste biomass samples without MWA. However, the use of MWA such as, solid carbonaceous absorbers, can result in improved product yields, composition and temperature at fairly low MW power.

9.2. Microwave assisted pyrolysis of waste biomass with solid carbonaeous absorbers

Bio-char was used to pyrolyze pelletized coffee hulls at fixed weight ratio and three increasing, but fixed MW powers. The biomass sample reached to 500 °C and 1000 °C at 130 W and 240 W respectively. The bio-oil yield increased from 7.90 wt% (at 500 °C, 130 W) to 9.19 wt% (at 800 °C, 270 W). However, increased power of 420 W decreased bio-oil yield to 8.58 wt% whereas, gas yield was found as high as 68.72 wt% at 1000 °C and contained much higher fraction of H_2 in syngas [75]. Salema and Ani [118] studied heating characteristics of Oil Palm Shell (OPS) with AC in original and modified single mode MW reactors at 50–600 W and 2.54 GHz. The modified cavity resulted in fairly high temperature 50–270 °C, whereas it was only 60–120 °C in original cavity of as received and 850 μm OPS under various operating conditions, but both cavities did not achieve pyrolysis condition. However, it was suggested that proper cavity design can produce pyrolysis conditions.

Salema and Ani [119] studied fluidized MWAP of OPS and Oil Palm Fiber (OPF) using bio-char (at 25, 50 and 100 wt%) and power level (100–1000 W) in modified MMW cavity. The use of 450 W and 50 wt% bio-char resulted in max. bio-oil of 22 wt% and 29 wt% gases from OPF, whereas 25 wt% and 30 wt% from OPS. The study espoused that as received OPS of size 0.001–0.1 m can be pyrolyzed using bio-char, which can reduce grinding cost. However, the surface and bed temperature of biomass sample varied significantly during fluidized MWH of OPS and OPF with bio-char during all operating conditions. Moreover, product yield and

temperature profile at various MW powers and bio-char loading are also lacking in this study. In order to improve uniformity of bed and surface temperature, Salema and Ani [55] used over head stirrer during MWAP of OPS with Coconut Activated Carbon (CAC). The use of over head stirrer and CAC increased pyrolysis temperature and heating rate, but it did not contribute to complete uniformity of surface and bed temperature. The study, however, suggested that the variation in surface and bed temperature is due to hotpots phenomena. The use of 450 W and 50 wt% CAC resulted in max. bio-oil of 17 wt%, which was lower than their pervious study using bio-char with OPS under comparable conditions [119], but contained higher phenol of 72% under GC–MS area. However, complete uniformity of surface and bed temperature during their study remained a challenge using over head stirrer.

The MWAP of oil palm empty fruit bunch pellets with CAC at 300 W and 450 W also resulted in significant variation between surface and bed temperature at low AC loading, but resulted in small variation at high CAC loading. The bio-oil was enriched in phenolic compounds of about 60–70 area% under GC–MS [120]. In continuation of efforts to achieve uniformity of temperature within pyrolysis sample and reduce bio-oil deposition within the reactor, Abubakar et al. [121] introduced simple pyrolysis technique during MWAP of OPS. This includes introducing inert gas from reactor top, which solved bio-oil deposition problem within MW reactor. The temperature profile, product yield and composition were all reported to be dependent on stirrer speed and CAC loading. More importantly, 450 W, 75 wt% CAC and 50 rotations per minute (rpm) resulted in uniformity of surface and bed temperature, which was attributed to uniform distribution of hotspots using lower stirrer speed. This new method improved bio-oil to 28 wt% and contained much higher phenol of 85% under GC–MS area using 75 wt% CAC and 100 rpm stirrer speed. It was suggested that phenol enriched bio-oil from this study can serve as potential alternative to petroleum based phenols.

In other study [122], AC was used as a MWA during MWAP of pelletized Douglas Fir (DF). DF to AC weight ratio was increased from 1.32 to 4.86 at fixed total loading of 120 g using fixed power of 700 W and varying time. The max. bio-oil of 48.1 wt% was obtained at 700 W, 350 °C and 4:1 AC to DF ratio. The studies suggested that optimum amount of AC to DF can result in maximum bio-oil and gas yields. It was also stated that reaction temperature and MWA to biomass ratios greatly affect bio-oil yield and composition. Moreover, the reaction time has less pronounced effects on product distribution.

Zhao et al. [123] carried out MWAP of wheat straw using pyrolytic residue in modified MW cavity at 3000 W. In addition to carrier gas, hot air was used to prevent condensation of vapors on the walls and pipelines for accurate analysis of bio-oil. The use of SiC as MWA with hot air affected the heating rate at different MW powers. The temperature reached 1000 °C using hot air of 200 °C at 900 W, which produced heating rate of 60 °C/min. However, in the absence of hot air, heating rate decreased with decreasing MW power. Furthermore, wheat straws to pyrolysis residue of 2:1 at three target temperatures resulted in small variation in bio-oil yield with 25 wt% (400 W) and 31 wt% (500 W and 600 W). However, the gas yield remained 25–31 wt%. The syngas concentration increased with increasing temperature. Jamaluddin et al. [124] optimized OPS char during MWAP considering reaction time, sample mass and N_2 flow rate. The carbon bed outside the pyrolysis medium was used to increase MW assimilation capacity of OPS. It was shown that three selected variables can affect calorific value, fixed carbon and volatile matter contents and yield percent of bio-char. Moreover, bio-char with low volatile matter and high calorific and fixed carbon value can be achieved using MWAP system.

To improve the quality of bio-oil, Bu et al. [125] investigated the behavior of four acid washed AC (coconut based, wood based,

bituminous coal and lignite coal) on pyrolysis oil and composition of DF sawdust pellets during MWAP. The use of four AC decreased the bio-oil yield compared to without AC, but lignite coal and wood based AC significantly increased phenols in bio-oil to 74.77% and 71.87% of GC–MS area, respectively, where it was only 2.54% of GC–MS area without AC. The study suggested that granular AC acted as catalyst and upgraded bio-oil in terms of phenol contents. Moreover, feasibility tests of two improved AC were demonstrated during recycle run. The recycle runs of DF with lignite coal indicated that phenol content in bio-oil from 1st run of 74.77% decreased to 54.39%, 45.2%, 48.1% and 26.8% of GC–MS after 2nd, 3rd, 4th and 5th runs, respectively; whereas the pattern was likely similar from wood based AC recycle runs. The product profile and composition of MWAP of waste biomass with carbonaceous MWA are summarized in Table 5.

9.3. Microwave assisted pyrolysis of waste biomass with inorganic and metal oxide additives

Chen et al. [126] investigated MWAP of pine wood sawdust with SiC and eight minor inorganic additives (NaOH, Na_2CO_3, Na_2SiO_3, NaCl, TiO_2, HZSM-5, H_3PO_4 and $Fe_2(SO_4)_3$) at 1000 W for 12 min, which resulted in maximum temperature of 470 °C. The untreated sawdust (without additives) resulted in 22.7 wt% of bio-oil and 60 wt% of gases. However, the additives decreased bio-oil yield compared to original sample, but $Fe_2(SO_4)_3$ resulted in maximum oil yield of 22.7 wt%. Bio-oil from untreated sawdust was mainly composed of acetol, furfural, 2-furanmethanol, 4-methyl-guaiacol, guaiacol and laevoglucose. Among the four sodium additives, NaOH showed increased selectivity towards acetol formation. H_3PO_4 and $Fe_2(SO_4)_3$ treated samples increased the formation of both furfural and 4-methyl-2-methoxy-phenol. However, TiO_2 and HZSM-5 showed no effects on acetol formation.

MWAP of corn stover and aspen wood pellets with metal oxides, salts, and acids as a MWA and additives at 875 W and 20 min resulted in temperature of 450–550 °C. However, increased bio-oil yield was observed using KAc, Al_2O_3, $MgCl_2$, H_3BO_3, and Na_2HPO_4. The use of 8 g of $MgCl_2$ per 100 g of corn stover and aspen resulted in 42 wt% of bio-oil and improved bio-oil product selectivity for furfural with 80% GC–MS area [72]. The catalytic effect of chlorides (NaCl, KCl, $CaCl_2$, $MgCl_2$, $AlCl_3$, $ZnCl_2$, $FeCl_2$, $FeCl_3$, $SnCl_2$, $CoCl_2$, NH_4Cl), metal oxides (MnO_2, ZrO_2, platinum alumina, Al_2O_3, MgO) and nitrates ($Mg(NO_3)_2$, $Fe(NO_3)_3$, $Cu(NO_3)_2$, $AgNO_3$, $Ni(NO_3)_2$, $La(NO_3)_3$, TeN_4O_{12}, $Rh(NO_3)_3$, $Co(NO_3)_2$) and $MgSO_4$ of 2 wt% with aspen pellets at 800 W and 2.54 GHz was investigated to improve bio-oil yield and quality. The use of metal oxides, $MgSO_4$ and chlorides particularly increased bio-oil yield to 41 wt% compared to 35 wt% without catalyst whereas, nitrates favored gas yield. The use of metal oxides enhanced the heavy oil yield, while $MgSO_4$ and chlorides favored water-phase residue in oil yield [127].

The influence of cotton stalks with NaCl, K_2CO_3 and $MgCl_2$ during MWAP resulted in decreased bio-oil yield with three additives. However, additives improved the quality of bio-oil in terms of acetic acid [73]. The use of four metal oxides (NiO, CuO, CaO, MgO) of 3 wt%, 5 wt%, and 10 wt% to sugarcane bagasse during MWAP at 500 W and 30 min resulted in slight increase in mass reduction ratio compared to without additives. Moreover, addition of CaO or MgO enhanced gas production and NiO or CuO favored liquid production [128]. To investigate the effects of catalyst characteristics, biomass conditioning, and reaction atmosphere, Huang et al. [129] used N_2 and CO_2 atmospheres to perform catalytic MW pyrolysis of corn stover with NiO, CuO, CaO and MgO at 3 wt%, 5 wt%, and 10 wt% at 500 W and 30 min. The influence of two different atmospheres on corn stover with metal oxides resulted in better reaction performance under N_2

than CO_2 environment, which was attributed to better heat absorbability of CO_2 molecules contributing to lower biomass temperature. The increased amount of metal oxides under N_2 conditions decreased reaction temperature, which was ascribed to compete between MW and energy absorption of catalysts and corn stover. Furthermore, metal oxides contributed to higher mass reduction ratio except MgO when compared to without additive under N_2 atmosphere. The liquid yield decreased using CO_2 compared to N_2 atmosphere. The aromatic detected in bio-oil using metal oxide catalysts was nearly similar in composition except CuO.

10. Co-utilization of coal and biomass resources

Biomass contains high alkali metal content due to its nutritional growth requirement. This inexpensive alkali metal source and relatively high surface area of biomass can be employed as a catalyst during co-utilization with coal [130]. In addition, biomass derived bio-fuels do not contribute to increase in atmospheric CO_2 emission since the amount of CO_2 consumed during biomass plant growth and produced during bio-fuels utilization essentially remains constant. Therefore, utilizing coal with biomass may reduce coal based CO_2 emission [131]. More importantly, co-utilization can reduce some important coal based pollutants such as, sulfur and nitrogen oxides (NO_x, SO_x), Poly Aromatic Hydrocarbons (PAHs), Volatile Organic Carbons (VOCs) and Total Organic Carbons (TOCs) [132]. The biomass catalytic activity showed net decrease in SO_x and NO_x emissions when biomass was co-fired with coal [133] and low ammonia yield when birch wood was co-gasified with Daw Mill coal [134]. Interestingly, the high contents of K, Na and Ca species in biomass improved some coal desulfurization features [135] and contributed to sulfur fixing potential in blended char by forming $CaSO_4$ and CaS [136]. Co-processing can also lead to different reactivities due to the difference in physicochemical properties of coal and biomass. The high volatile matter content of the biomass can facilitate conversion and upgrade fuel components during co-processing with coal. In brief, co-processing can not only reduce the coal based pollutants, but a step forward toward clean coal utilization [137].

10.1. Conventional co-gasification of coal and biomass

Valero and Usón [138] utilized coal gasification plant data to model co-gasification system. It was suggested that the predicted co-gasification model for coal, coke with up to 10% of different biomass types (wheat straw, barley straw, pine wood, olive tree, wine tree and cynara) can be effectively applied to operate co-gasification of fuel mixture. Cormos [139] proposed that co-gasification plant model data of coal and other alternative fuels (mainly biomass feedstock) blends can result in net zero fossil CO_2 emissions. Co-gasification of coal with biomass is a promising technology to reduce coal based CO_2 emissions and observe synergy (i.e. chemical interaction between coal and biomass particles) in volatile and gas phase species. Collot et al. [140] observed no synergy in terms of total volatiles and tar yield when bituminous coal and silver birch wood were co-gasified by intimate mix and segregated contact in fixed bed and fluidized bed reactor under helium and CO_2 atmosphere at pressure of 0.1–2.5 MPa and 850–1000 °C. It was suggested that the biomass-char formed at high temperature can contribute to some catalytic effects. In another study [134], the fluidized co-gasification of brich wood with Daw mill and Polish coal in oxygen enriched nitrogen atmosphere at 0.4 MPa and 700 °C and 900 °C was reported to increase reaction rate and gas production of blends compared to predicted blend suggesting blended char reactivity due to the presence of biomass mineral content. Moreover, low tar and ammonia yield were also identified towards synergy. Brown et al. [141]

used the biomass based alkali potassium salt (pure K_2CO_3 as additive) during co-gasification of switchgrass and Illinois coal in Thermogravimetric Analyzer (TGA). Coal–char in the presence of K_2CO_3 showed increased gasification rate compared to blended char and coal char alone. Moreover, it was indicated that addition of K_2CO_3 with switchgrass ash and coal char of 1:1 increased gasification rate by eight-fold at 895 °C.

Pan et al. [142] reported improved gasification efficiency of blended Sabero and black coal with pine chip during co-gasification in continuous fluidized bed reactor operated at 840–910 °C and 0.14 MPa under air–steam environment. Zhu et al. [143] studied the effects of alkali salts on wheat straw and coal particles in TGA and fluidized system. It was reported that the blended char showed high gasification reactivity compared to coal–char alone. Moreover, acid washed wheat-char and coal–char showed similar reactivity indicating that blended char demonstrated high reactivity due the presence of biomass high alkali content. Kajitani and co-workers [144] tested the co-gasification reactivity of cedar bark and two types of coal at high temperature of 1400 °C in drop tube furnace and TGA at 850 °C and 950 °C under CO_2 atmosphere. They observed low temperature synergy with no synergy at high temperature. The low temperature synergy was reported to improve gasification reactivity, which was espoused to presence of biomass alkali and alkaline salts. The increased catalytic effects of alkali metal in biomass during co-gasification with coal were also observed by McKee et al. [145] and Srivastava et al. [146]. In general, blending coal with biomass provides high gasification reactivity and synergetic effects due to the presence of biomass mineral catalytic effects.

Several researchers have studied the effects of coal and biomass fuel blends on H_2, CO_2 and CO production [142,147–151]. These studies observed decrease in H_2 and increase in CO_2 and CO production when biomass in fuel blend is high. The decrease in H_2 content was ascribed to the presence of high volatile matter in biomass, which reduces gasification temperature leading to low hydrogen production, whereas high biomass-char reactivity and high biomass oxygen content favor CO_2 and CO production. Pinto et al. [152] studied the effects of temperature 750–890 °C during co-gasification of pine biomass and coal. It was concluded that increased temperature can promote hydrocarbon reaction with decrease in tar yield from blended char compared to coal alone. Kumabe et al. [148] observed slight decrease in tar yield during co-gasification of coal and Japanese cedar with air and steam in fixed-bed downdraft gasifier operated at 900 °C. Emami Taba et al. [153] reviewed the effects of temperature on the fuel gas composition of gasification and co-gasification of coal and biomass blends. Several researchers considered the effects of temperature on fuel gas composition during co-gasification of biomass and coal [151,152,154–156]. These studies observed increased H_2 and CO production and decreased CO_2 and CH_4 concentrations with the rise in temperature, which was espoused to promote endothermic gasification reactions at high temperature. The effect of pressure on co-gasification of biomass and coal and its products has not been studied in detail.

Most co-gasification studies mainly focused towards parametric studies with much less attention on how coal and biomass particles behave and degrade during thermal utilization in isolation and mixture. The thermal gasification behavior of coal and biomass in isolation and char produced at various temperatures and its effects on volatile/tar yield and composition need special attention with emphasis on variations in char morphology, which can help to understand co-gasification performance of coal and biomass blends.

10.2. Conventional co-pyrolysis of coal and biomass

Early co-pyrolysis studies on coal and biomass mostly concentrated on the mechanism of gas production and reported absence of synergetic effect in the gas phase species [140,157,158]. These

Table 6
Review of conventional co-pyrolysis studies of coal and biomass resources.

Components	System/reactor	Operating parameters	Findings	Ref.
Black coal, waste coal, Pine chips	Thermo-balance apparatus	Various coal–biomass blends, dynamic temperature conditions of 110–900 °C, heating rate 100 °C/min, N_2 gas at atmospheric pressure.	Additive behavior and no synergetic effects in blends.	[158]
Daw mill coal, polish coal, silver birch wood, forest residue	Fixed bed (intimate contact) and fluidized bed (segregated contact)	Helium and CO_2 as sweeping gases, temperature 850–1000 °C.	Both reactors appeared lack of synergetic effects during blends.	[140]
Sub-bituminous coal, pine saw	Static batch reactor	Blending ratio 5%, 7.5% and 10%, 150–700 °C, heating rate 5–80 °C/min, N_2 as sweeping gas.	Blends showed lower temperatures due to low degradation temperature attributed to biomass cellulosic components.	[174]
Coal, pine sawdust	Horizontal fixed bed tubular reactor	Pine sawdust–coal blends, temperature 200–1400 °C, low and high heating rates, N_2 as sweeping gas.	Additive fuel behavior.	[159]
Coal, sawdust, olive stones, additives (calcium hydroxide and lime stone)	Fixed bed reactor	Various blends of biomass and coal, heating rate 10 °C/min, Argon at 86 mL/min.	Synergetic effects in terms of H_2S gas loss during blends with advantage to reduce sulfur content of coal.	[161]
Coal, wood waste/wheat straw	Thermo-gravimetric apparatus	Coal to biomass ratio (10:90, 20:80, 30:70, 50:50), heating rate 20 °C/min, N_2 as sweeping gas.	Absence of synergy.	[160]
High sulfur coal, olive stones, wheat straw, almond shells, pine sawdust	Thermo-gravimetric system and mobile pilot plant bed system	TGA: non-isothermal system: final temperature 900 °C, heating rate 10 °C/min, N_2 at 120 mL/min Mobile bed system: temperature 600 °C, N_2 at 2 L/min, 2 h of residence time.	Twice sulfur loss at high biomass to coal blend ratio with improved coal de-sulfurization feature.	[135]
Three coal types, pinewood	Thermo-gravimetric analysis	Coal and biomass blends, temperature 900 °C, heating rate 25 °C/min.	Additive behavior.	[163]
Lignite, legume straws	Free fall reactor	Blending ratio 0–100 wt%, temperature range 500–700 °C.	Char-gas interaction at high blending ratio.	[137]
Peat, lignite, bituminous coal, reed	Thermo-gravimetric analysis	Peat blend with reed, lignite and bituminous coal 80:20, 60:40, 40:60, 20:80, temperature 25–900 °C, N_2 at 50 mL/min.	Peat, lignite, bituminous coal, reed and blends showed dissimilar pyrolysis characteristics. For reed alone, pyrolysis takes place in one stage. For lignite–reed blends pyrolysis occurred in two stages. Blends of reed with bituminous coal occurred in two to four stages.	[168]
Lignite, hazelnut shells	Thermo-gravimetric analysis	Lignite/biomass ratio of 98:2, 96:4, 94:6, 92:8, 90:10, and 80:20, temperature ambient to 900 °C, linear heating rate of 20 °C/min under dynamic N_2 flow of 40 mL/min.	Synergy between 127 and 327 °C, above 327 °C no synergy. Addition of hazelnut shell to lignite contributed to sulfur fixing in blended char forming CaS and $CaSO_4$.	[136]
Coal, wheat straw	Thermo-gravimetric analysis and gasification topping process	Blending ratio 100:0, 80:20, 70:30, 50:50 and 0:100, coal and wheat straw dried at 110 °C for 4 h and 1 h, temperature 900 °C, isothermal conditions, heating rate 40 °C/min, isothermal gasification reaction with char samples at CO_2 flow of 70 mL/min	Bio-chars showed high gasification reactivity than coal–char. Results indicated that co-pyrolysis char at 750 °C has the highest alkali concentration and reactivity.	[143]
Lignite, waste wood fines	Thermo-gravimetric analysis	Coal and biomass dried at 100 °C for 2 h. Blending ratio 100:0, 50:50, 40:60, 10:90, and 0: 100, slow heating rate of 40 °C/min, N_2 flow of 0.1 L/min.	Absence of synergy.	[167]
Sub-bituminous coal, bituminous coal, sawdust	Thermo-gravimetric analysis	Coal–sawdust blend 50:50, temperature ambient to 1200 °C, heating rate 10, 30 and 50 °C/min, N_2 100 mL/min.	Interaction effects in blends above 400 °C attributed to secondary reactions inhabiting char formations.	[170]
Sawdust, sub-bituminous coal	Thermo-gravimetric analysis and fixed bed reactor	TGA: sawdust to coal ratio of 0.4, temperature 900 °C, heating rate 15 °C/min, N_2 at 200 mL/min at 1.2 bars. Fixed bed reactor: six blending ratio (sawdust ash/(sawdust ash+coal)) 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 pyrolyzed at identical conditions, N_2 at 0.2 m/s for 30 min.	Yield and conversion of co-pyrolysis blends was higher than the individual experiments. In TGA, weight loss for blends increases above 400 °C and additional weight loss at 700 °C. In fixed isothermal bed, synergy is observed at blend ratio of 0.4. The synergies reported towards gasification.	[175]
Coal (peat, lignite, bituminous and anthracite), Hazelnut	Thermo-gravimetric analysis	Each coal/hazelnut blends 10:1, temperature ambient to 900 °C, non-isothermal experiments, heating rate 40 °C/min, N_2 at 40 mL/min.	Addition of hazelnut to coal produced some increase in de-volatilization rates below 500 °C. Blended char showed unexpected variations in the case of low rank coals. Synergy towards increase in char.	[169]
Brown coal, bituminous coal, legume straw, pine sawdust	Laboratory scale freefall reactor	Sample dried for 2 h at 105 °C, blending ratio 0–100%, temperature 500–700 °C, heating rate 500 °C/s, vacuum pump with N_2 (35 cm^3/min) as a balance gas, residence times < 2 s.	Synergy at short-gas-residence time.	[176]
Coal (bituminous, anthracite), rice straw, chinar leaves, sawdust, pine sawdust	High-frequency magnetic field furnace	Six biomass to coal blends (1:4 wt %), 600–1200 °C, argon 500 mL/min.	Synergy on char-nitrogen yields in blends. Synergies increased volatile-nitrogen yields, but decreased (NH_3+HCN) yield. HCN formation promoted at 600–700 °C.	[177]
Coal from various locations, pine sawdust, Oat straw	Thermo-gravimetric analysis	Varying coal rank and biomass blends, 900 °C, heating rate 25 °C/min, N_2 flow	Small effects on pyrolysis rates during blends with no gross changes during de-volatization.	[171]
Bituminous coal, switch grass	Drop tube reactor	Blending ratio of coal to biomass 100:0, 50:50, 70:30, 85:15, and 0:100; temperature 900 °C; atmospheric pressure, argon flow rate of 2000 standard cubic centimeter.	Lack of synergy.	[164]

Table 6 (*continued*)

Components	System/reactor	Operating parameters	Findings	Ref.
Bituminous coal, rice straw	High frequency furnace	Samples dried 105 ºC for 1 h, biomass to coal blends (1:4, 1:1, and 4:1), argon 500 mL/min.	Synergies at biomass to coal ratio of 1:4 decreased char and increased volatile yields. Synergies during gasification.	[173]
Coal, bagasse, corn cobs, corn stover	Thermo-gravimetric analysis bagasse and corn residue blended with coal	Samples air dried for 48 h; biomass to coal ratio 90:10, 80:20, 70:30, 60:40 and 50:50; heating rates for single fuel 5, 10, 20, 30, 40, 50 and 150 ℃/min and blends at 5, 10, and 50 ℃/min.	Co-pyrolysis caused variability in activation energy of blends compared to single fuel. Non-additive or synergetic behavior.	[172]

studies paid much less attention towards synergetic effects on the pyrolysis product composition. The synergic effects of coal–biomass blends on the yield of major pyrolysis products, particularly to volatile matter, have been studied [159–166]. These studies also reported lack of synergies. However, synergies in terms of improved coal de-sulfurization features [135,161] and sulfur fixing potential [136] were observed. The volatiles from coal and biomass blends were reported to produce very small synergy over specific temperature range, but additive behavior was observed beyond the temperature range [136]. Moreover, the synergetic effects in blends under various process conditions were not successful [135,140,158–160,163,164,167]. Moghtaderi et al. [130] reported that coal and biomass blends showed decreased pyrolysis temperature, which was espoused to low thermal degradation temperature of waste biomass cellulosic content. Moreover, the blends produced synergy in terms of decreasing the char and tar yield, but resulted in increased gas yield. Most co-pyrolysis studies were demonstrated in TGA reactors [135,136,143,158,160,163,167–172], fluidized bed reactors [140,158] and entrained bed reactors [137]. The survey of various conventional co-pyrolysis studies conducted on coal and biomass resources is summarized in Table 6.

Fixed-bed TGA reactors provide good contact of coal and waste biomass particles during co-pyrolysis studies, but at low heating rate. The high heating rate can be achieved using fluidized or entrained bed reactors, but dispersions of coal and waste biomass particles can result in very slight synergies. Therefore, conventional fixed-bed, fluidized and entrained bed reactors may not be suitable to investigate the synergetic effects during co-pyrolysis conditions [173]. The lack of synergy may be attributed to conventional co-pyrolysis heating systems. The coal requires sufficiently higher temperature for de-volatilization compared to waste biomass. More importantly, the volatiles from waste biomass will be released at lower temperature and subsequently leaves the conventional reaction system, while the volatiles from coal will be released at higher temperature. Therefore, conventional co-pyrolysis heating systems are unable to achieve strong synergy in the vapor phase.

11. Microwave assisted pyrolysis factor considerations and concerns

The choice of process variables and suitable range is the most important stage to improve product yield and selectivity, which may not only depend on the number of significant factors but also the availability of resources to control these variables. Several factors were identified during the literature review of MWAP of coal and waste biomass by analyzing their association on heating rate, pyrolysis temperature, product yield and composition. These factors are summarized in Table 7 along with their MWAP considerations and concerns.

12. Future directions

The energy scarcity from conventional fossil fuels demands interest in sustainable and renewable fuels; and with increased demand of liquid fuels, synthetic fuels from coal and waste biomass resources can become a promising option to supplement conventional fossil fuels. The energy recovery from waste biomass has gained considerable attention to obtain value-added chemicals, fuels and gases. The integration of microwave technology to fast pyrolysis provides a challenging environment to treat various biomass materials, which can improve liquid and gas fuels. Microwave fast pyrolysis of biomass with carbonaceous, inorganic and metal oxide microwave absorbers has shown low temperature energy efficient route to improve product selectivity and recovery of valuable fuel gas components (particularly H_2 and syngas). However, there is a strong need to explore more conventional and non-conventional surface modified microwave absorbers to investigate the product selectivity from waste biomass. Moreover, due to the increased utilization of microwave absorber with waste biomass, there is a strong need to evaluate dielectric properties of potential biomass feedstock and absorbers. The choice and application of the absorbers with low loss organic material primarily depend on dielectric properties of feedstock and absorber, applied microwave power and frequency, and penetration depth at process temperature. The penetration depth of pyrolysis material at 2.54 GHz needs proper attention to design an energy efficient multimode microwave pyrolysis system since it controls the distribution of microwave within the material. The addition of absorber to pyrolysis material is supposed to influence penetration depth and optimum bed thickness of pyrolysis material with absorber needs to be evaluated at the initial stages due to non-availability of sufficient penetration data of pyrolysis material with absorber medium. The non-uniform distribution of receptor with low loss material and uneven dependence of microwave energy during multimode microwave can result in hotspots phenomena and deteriorate reaction mechanism, which can influence product yield and selectivity. The distribution of absorber with pyrolysis material can play an important role to minimize localized heating, which can improve product yield and selectivity. The motivation to use waste biomass with coal is growing. Researchers around the world are focused on how to exploit waste biomass high volatile matter and alkali metal content to upgrade fuel components when co-utilized with coal. The conventional co-utilization of coal and biomass resources through co-gasification and co-pyrolysis routes offers some benefits over SO_x and NO_x reduction, but most studies observed additive fuel behavior in blends and were unable to achieve strong synergies in gas and vapor-phase species. It was established that microwave assisted pyrolysis of coal and biomass in isolation offers number of advantages over conventional pyrolysis method. Despite improved heating nature and fuel recovery from microwave assisted pyrolysis of coal and biomass in the presence of solid microwave absorber, most co-pyrolysis and co-gasification studies remained limited to conventional heating methods only. The heterogeneous gas-phase reactions such as catalytic CH_4 decomposition, and dry CO_2 and CH_4 reforming reactions over carbon surface have been found effective for H_2 production under MW irradiation conditions. It is therefore proposed that microwave assisted co-pyrolysis of coal and biomass over carbon surfaces is considered effective for gas and

Table 7
Microwave assisted pyrolysis factor considerations and concerns.

Factor category	Factor name	Considerations	Concerns
Waste biomass and coal	Type	– Essentially no pretreatment of feedstock – Affects product yield, quality, heating rate and final temperature due to variation in physiochemical properties of biomass and coal	– Detail assessment of physiochemical properties of biomass and coal – Behavior of biomass and coal in isolation and mixture during microwave pyrolysis system
	Particle size	– Very small particle shows minimal effects on heating rate and final temperature – Both small and large particles require sufficiently high microwave power to improve pyrolysis temperature without microwave absorber	– Energy consumption for grinding – Requires sufficient microwave power to reach pyrolysis temperature without microwave absorber
	Moisture content	– Inherent moisture content improves heating rate at initial microwave heating stage	– Separation of water/oil mixture
Microwave absorber	Type	– Catalytic effects on product yield and its quality due to type of absorber used – Contribute to heating rate – Increases microwave assimilation capacity and final pyrolysis temperature of bulk material – Requires low microwave power to treat material with high dielectric loss microwave absorber	– Hotspots phenomena resulting in thermal instability of material due to uneven distribution of microwave absorber, variations in microwave field and in thermo-chemical properties of material – Choice and distribution of suitable microwave absorber – Reuse and regeneration of microwave absorber
	Particle size	– Large microwave absorber particle may contribute to non-uniform mixing with material, which can result in increase hotspots and uneven temperature profile within material – Conversely, small particle may reduce hotspots and contribute to uniform heating of bulk material due to increased surface area of absorber	– Separation of microwave absorber and material
	Microwave absorber loading	– Catalytic effects on product yield and its quality due to vapor–gas contact with microwave absorber – Contribute to heating rate and final pyrolysis temperature – Increases hotspots at low loading and vice versa – Effects microwave penetration depth at high absorber loading	– Optimization of microwave absorber loading – Optimization of microwave penetration depth
Reactor configuration	Microwave output power	– Contribute to heating rate and final pyrolysis temperature – Uneven heating of material due to on–off and fluctuating nature of multimode microwave heating – Low power increases process time at slow heating rate and vice versa	– Optimization of microwave power – System design for microwave power control to provide suitable heating rate and process temperature
	Microwave time Mixing	– Contribute to process heating – Non-uniform mixing of absorber with material can result in hotspots and uneven heating within the material – Agitation and rotating the material can contribute to even distribution of microwave energy and uniform heating	– Suitable process heating – System design for even distribution of microwave energy within the material
	Inert gas flow rate	– High flow rate reduces vapor–gas interaction with absorber, which can affect product yield and quality, and vice versa – High flow rate increases heating carrying capacity of reaction bed – Low flow rate increases the chances of volatile sticking on the reactor wall – Heating carrying capacity depends on type of inert gas used	– Choice of inert gas and optimization of inert gas flow rate – System design to control process temperature

vapor-phase synergies. The selective and improved fuel recovery from continuous microwave assisted pyrolysis and co-pyrolysis of coal and biomass with microwave absorber can attract considerable attention in commercial applications. The development and testing of conventional and non-conventional surface modified catalytic microwave absorbers will help to drive the field forward and set new avenue.

13. Conclusions

Microwave pyrolysis of organic material without microwave absorber requires sufficiently high microwave power to attain pyrolysis conditions and result in broad spectrum of chemicals in bio-oil, which needs additional units to recover valuable chemicals. The presence of specific microwave absorber with organic material provides one step in-situ upgrading of pyrolysis vapors to improve product selectivity. Microwave assisted pyrolysis has been demonstrated as a promising alternative to conventional pyrolysis. However, critical comparison of two systems has shown that microwave heating requires the presence of microwave absorber, whereas no such material has been demonstrated to increase heat absorption and catalytic capacity of material in conventional pyrolysis. Therefore, direct comparison of two systems is not appropriate. The motivation to use biomass with coal is an attractive option to reduce CO_2 emission and step forward towards clean coal utilization. It is

assumed that the high alkali metals and volatile matter content present in the biomass can produce synergy by upgrading fuel components when co-utilized with coal. The catalytic effects of biomass alkali metals content have been observed to increase gasification rate when co-gasified with coal in conventional system. The synergetic effects of coal–biomass blends on the yield of major pyrolysis products, particularly to volatile yield, have shown additive fuel behavior in conventional pyrolysis system.

Acknowledgments

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